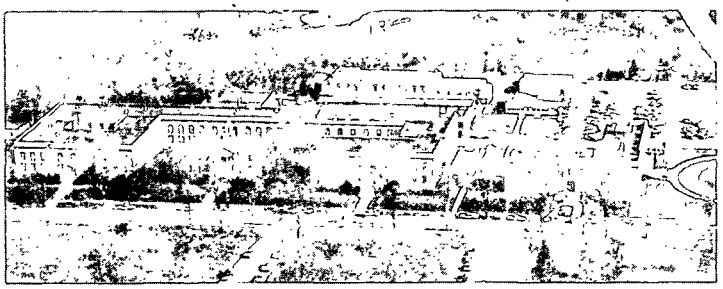

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# PHOTOCHEMISTRY OF CARBOHYDRATE MODEL COMPOUNDS. I. KETONE INITIATED HYDROGEN ABSTRACTION REACTIONS OF 2-METHOXYTETRAHYDROPYRAN

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# PHOTOCHEMISTRY OF CARBOHYDRATE MODEL COMPOUNDS. I. KETONE INITIATED HYDROGEN ABSTRACTION REACTIONS OF 2-METHOXYTETRAHYDROPYRAN

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ABSTRACT

The reaction of 2-methoxytetrahydropyran with ketones under the influence of ultraviolet light was studied as a model for carbohydrate degradation. The two major "carbohydrate" products were methyl valerate and δ-valerolactone. With benzophenone in benzene, methyl 5-phenylvalerate was also formed. Two mechanistic pathways involving the 2-methoxytetrahydropyran-2-yl radical can account for the products. The relative importance of the two pathways was found to be a function of the ketone and solvent.

## INTRODUCTION

The study of the photochemical reactions of carbohydrates is complicated by several factors. Most of the compounds have little or no absorbance in the accessible ultraviolet. This leads to the possibility of sensitized reactions originating from chromophoric impurities. The polyfunctionality of these materials gives rise to a large number of sites of comparable reactivity, giving complex product mixtures. In addition, many of the photoproducts absorb light more strongly than the starting materials and, therefore, secondary reactions can obscure primary processes.[1]

Further frustrating efforts to understand the basic processes taking place is the fact that a wide variety of conditions have been employed in work reported in the literature.[2] Researchers interested in textiles are concerned with the effect of dyes on the photochemistry of cellulose.[3] Others have studied the effects of inorganic additives on carbohydrate photochemistry.[4] In most cases, oxygen is present in the system, which promotes more rapid reaction, but also leads to extensive degradation, in some cases all the way to carbon dioxide.[1]

In many instances, authors report working with materials which show a weak absorption maximum at 260-280 nm.[5] This has been ascribed to both the open chain, carbonyl form of the compounds[6] and also to an absorption band of the "acetal chromophore" itself.[7] Our experience has been that most commercial samples of carbohydrates show absorption in this region but, in most cases, careful recrystallization can completely remove the absorbing impurities. One might infer from this that impure samples have been used occasionally in the past. This conclusion was also reached by Bos.[8]

The most reasonable impurities would be carbonyl compounds, the absorption being due to the $n \rightarrow \pi^*$ transition. Such groups are almost certainly present as irregularities in cellulose.[8] It was with these considerations in mind that we decided to examine the photochemistry of 2-methoxytetrahydropyran (MeOTHP), a model for a glycoside, in the presence of ketones.

A previous report[9] of the reaction of MeOTHP, benzophenone, and benzene in the presence of ultraviolet light gave the major products as δ-valerolactone and methyl valerate (Eq. 1), formed in a ratio of 16:1 and a total yield, based on starting material consumed, of 41%. This product ratio seemed surprising since one would expect that the loss of methyl radical (path A, Eq. 2) from the proposed intermediate 2-methoxytetrahydropyran-2-yl radical would be less favorable

than the loss of the primary alkyl radical (path B) based on relative radical stabilities whereas the reported product ratio indicated the opposite. Furthermore, di-t-butyl peroxide was reported to give methyl valerate as the major, volatile product in a thermal reaction and no valerolactone was found.[10]

[Cut 1 and 2 here]

In this paper, we would like to report: 1) the finding of another, major photoproduct in the above benzophenone, benzene system which indicates that path B is the major pathway; 2) a solvent effect in going to t-butyl alcohol favoring path A; and 3) a change in product distribution in changing the initiator from benzophenone to acetone.

RESULTS

Irradiation of MeOTHP in the presence of acetone or benzophenone and in the absence of oxygen led to the production of δ-valerolactone and methyl valerate. In addition, with benzophenone in benzene, methyl 5-phenylvalerate was a major product. This product was not identified in the previous report.[9] The results (Table I) indicate that the product distribution is a function of both the solvent and the ketone.

[Table I here]

The products were identified by comparison of v.p.c. retention times on at least two different columns and infrared or n.m.r. spectra of samples collected from the v.p.c. column with those of authentic materials. Quantitative results were obtained by v.p.c. and assumed a molar flame ionization response proportional to molecular weight.

In addition to these major products, several other, minor products showed up in the chromatograms but, with the exception of biphenyl in Irradiation 4, were not identified. Biphenyl was identified only by retention time on two columns. Also, some relatively nonvolatile products must have formed in some cases, since not all of the starting material could be accounted for by the observed products. These minor products varied, both in amount and retention time, with the reaction conditions.

The difference in major product ratio might a priori be attributed to a lack of stability of methyl valerate and/or δ-valerolactone in the benzophenone and acetone systems, respectively. However, in control experiments these products were found to decompose to the extent of only 15% or less, even when irradiated for the full time of the MeOTHP irradiations. Since these products were gradually formed during the MeOTHP irradiations, the average exposure to the reaction conditions would have been less than in the control experiments. Therefore, product instability cannot account for the difference.

## DISCUSSION

The mechanism previously proposed[9,11] and shown in part in Eq. 2, accounts for δ-valerolactone and methyl valerate. In addition, the methyl 5-phenylvalerate found in Irradiation 4 can be accommodated by the mechanism by reaction of the methyl valer-5-ylate radical with the benzene solvent as shown in Eq. 3.

[Cut 3 here]

Thus, methyl valerate and methyl 5-phenylvalerate both derive from the ring opening path B shown in Eq. 2. Path B, therefore, accounts for 78% of the identified products in Irradiation 1 and 67% in Irradiation 4. In Irradiation 3, however, path B accounts for only 30% of the observed products.

No explanation of the lack of reaction in the acetone-benzene system (Irradiation 2) comes to mind. The ketone is absorbing essentially all of the UV light transmitted by the pyrex vessel in both Irradiations 2 and 4. Also, benzene is known to be ineffective in quenching the triplet state of actone in the gas phase.[12]

Comparison of Irradiations 1 and 3 indicates that the ketone can have an effect on the product distribution. Comparison of Irradiations 3 and 4 indicates that the solvent can also influence the reaction.

There are several possible rationales for these effects. The formation of relatively nonvolatile products via radical coupling reactions could account for the differences. Although dimethyl sebacate was not formed in amounts greater than 1% in these irradiations, as shown by v.p.c., coupling of the open-chain radical with the ketyl radical formed from benzophenone in Irradiation 3 is a possibility.

A second rationale is that Path B is potentially reversible whereas Path A is not. The lifetimes of the various intermediates may well vary in the different media and the importance of this reversibility could thus change.

Finally, conformational effects could be important. Although the conformational composition of MeOTHP did not change much in going from benzene to t-butyl alcohol (see Experimental Section), the conformations involved in the product forming steps could be stabilized to differing degrees in the various media.

We are presently looking at conformationally rigid, diasteriomeric model systems to test these hypotheses.

## EXPERIMENTAL

### Starting materials

Reagent-grade benzene was stirred with sulfuric acid and distilled. Tertiary butyl alcohol was refluxed with and distilled from calcium hydride. Acetone was distilled from potassium permanganate. Benzophenone was recrystallized twice from 95% ethanol. 2-Methoxytetrahydropyran was prepared by the method of Woods and Kramer.[13] No impurities were detected by n.m.r. or v.p.c.

### Irradiations

Irradiations were carried out in a Rayonet Photochemical Reactor (Southern New England Ultraviolet) with RPR 3000 lamps using pyrex tubes as filters. This assured that only ketones were absorbing light. Dilute solutions (see Table II) were deoxygenated by bubbling nitrogen through the solution for 20-30 min prior to and during irradiation or by at least three freeze-pump-thaw cycles followed by sealing the tube *in vacuo*.

[Table II here]

### Control experiments

Two solutions were prepared, degassed by three freeze-pump-thaw cycles, sealed *in vacuo*, and irradiated as above for 21 hr. The first solution, composed of 0.180 g of valerolactone, 1.6 g of acetone, and 18 ml of *t*-butyl alcohol, showed 84% of the original valerolactone concentration and no new peaks in the gas chromatogram after irradiation. The second solution consisted of 0.089 g of methyl valerate, 0.184 g of benzophenone, and 20 ml of benzene and showed 88% of the original methyl valerate concentration and a new peak corresponding to 12% of the original methyl valerate concentration.

Product analysis

Products were identified by preparative v.p.c. followed by spectral comparison with known samples. Methyl valerate was identified by n.m.r. spectroscopy while δ-valerolactone and methyl 5-phenylvalerate were identified by infrared. All compounds showed retention times identical to authentic samples on two or more v.p.c. columns. Biphenyl was identified in Irradiation 4 by retention time only.

Quantitative analysis was carried out by v.p.c. A molar response proportional to molecular weight was assumed for the flame ionization detector for the identified products. Unidentified, minor products were assumed to have a response equal to that of MeOTHP. Columns used were: 10% Carbowax 20M on 60/80 Chromosorb W, 1/8" x 6'; 20% Carbowax 1500 on 100/120 Gas Chrom Q, 1/8" x 20'; 3% OV-17 on 100/120 Gas Chrom Q, 1/8" x 4'. Preparative v.p.c. was done on 5% SE-30 on 60/70 Anakrom ABS, 1/4" x 5'.

N.m.r. analysis of the conformation of 2-methoxytetrahydropyran

N.m.r. spectra of MeOTHP were run in benzene and t-butyl alcohol. The signal for H-2 ("anomeric proton") was then used to determine the axial: equatorial ratio according to the method of Pierson and Runquist,[14] who determined the ratio for neat MeOTHP. The distance between the outer peaks (shoulders) of the broad triplet was 5.5 ± 0.5 Hz in benzene and 6.5 ± 0.5 Hz in t-butyl alcohol. These values correspond to 86 ± 10% and 69 ± 10% axial methoxy, respectively. Pierson and Runquist found a value of 72% for the neat liquid.

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TABLE I

COMPOSITION OF SOLUTIONS AFTER IRRADIATION[a]

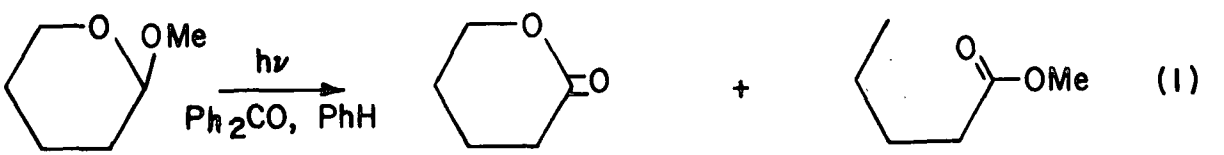
| Irradiation[b] | Sensitizer | Solvent | MeOTHP | MeVal[c] | Val[d] | MePhVal[e] | Minor[f] |
|---|---|---|---|---|---|---|---|
| 1 | Acetone | t-BuOH | 53 | 18 | 5 | -- | 14 |
| 2 | Acetone | benzene | 100 | 0 | 0 | 0 | 0 |
| 3 | Benzophenone | t-BuOH | 64 | 3 | 7 | -- | 0 |
| 4 | Benzophenone | benzene | 58 | 7 | 14 | 22 | 10[g] |

[a] V.p.c. analysis of products at least as volatile as benzophenone (mole percent of original MeOTHP concentration).
[b] See Table II for details.
[c] MeVal = methyl valerate.
[d] Val = δ-valerolactone.
[e] MePhVal = methyl 5-phenylvalerate.
[f] Minor products not identified; yield based on original MeOTHP concentration.
[g] Includes 3% biphenyl.

TABLE II

IRRADIATIONS

| Irradiation | Solvent (ml) | Ketone (g) | MeOTHP (g) | Time (hr) |
|---|---|---|---|---|
| 1 | t-BuOH (18) | Acetone (1.6) | 0.628 | 21 |
| 2 | Benzene (18) | Acetone (2.4) | 0.585 | 36 |
| 3 | t-BuOH (20) | Benzophenone (0.185) | 0.122 | 16 |
| 4 | Benzene (20) | Benzophenone (0.188) | 0.118 | 19 |

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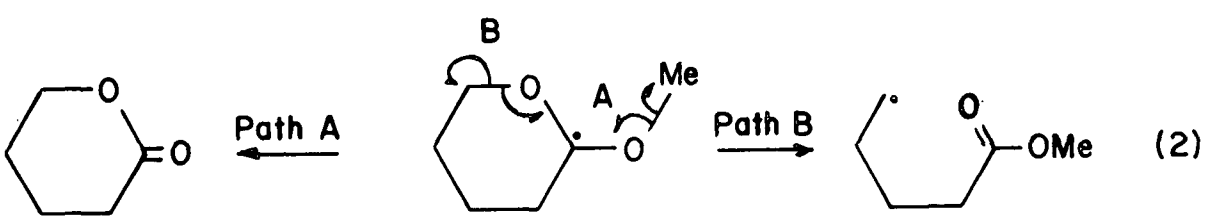


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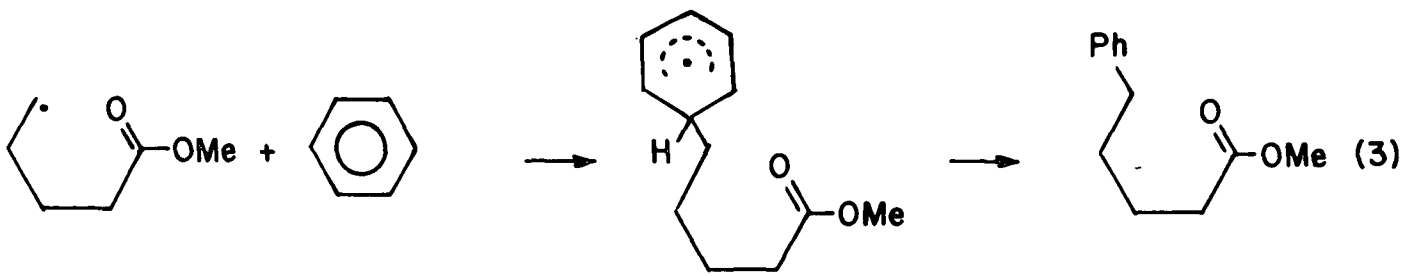


(3)

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